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Electronic states of elongated PbSe/PbS Core/shell quantum dots

T Walsh[1], J Miloszewski[1], U Aeberhard[2] and S Tomić[1]

[1]University of Salford, Greater Manchester, United Kingdom
[2]IEK-5 Photovoltaik, Forschungszentrum Jülich, Germany

Abstract. The optical characteristics of colloidal quantum dots (QDs) are highly dependent on the physical geometry of the QD (size, shape) as well as composition. These dependencies make such systems attractive for application in novel optical devices, notably for solar cell technology. Empirical electronic structure methods, such as $\boldsymbol{k}\cdot\boldsymbol{p}$ theory, or empirical pseudopotential theories have successfully reproduced experimentally observed transitions in CdSe and PbSe colloidal QDs. Our approach uses the $\boldsymbol{k}\cdot\boldsymbol{p}$ method to predict such properties as the electronic structure and dipole transitions of ellipsoidal PbSe/PbS core/shell structure colloidal QDs, as a function of eccentricity. Due to the anisotropy between the longitudinal (*z*) and transverse (*x* and *y*) directions, we present results from elongation along both the x and z directions.

1. Introduction

The current generation of solar cell devices, based on single gap bulk semiconductor materials, have a maximum theoretical efficiency, known as the Shockley-Queisser limit [1], based on the principle of detailed balance, typically in the range of 30%-40%. It was suggested that nanocrystal quantum dots, also known as "artificial atoms", may be used to overcome this limit [2]. The tunable nature of the QDs (through growing crystals of appropriate size, shape and composition) allows for the selection of band gap energies, as well as associated electronic and optical properties. It is therefore desirable to develop a theoretical framework with which to predict and explore these properties. In the current work, we present our findings on the effect of eccentricity on electronic and optical properties for PbSe/PbS core/shell colloidal QDs, for elongation in both longitudinal (z) and equivalent transverse (x, y) directions, along with the methodology used when performing calculations.

2. Methodology

In the non-interacting electron level of theory, the four–band $\boldsymbol{k}\cdot\boldsymbol{p}$ Hamiltonian, expanded in the $|L_6^-;\alpha\rangle$, $|L_6^+;\beta\rangle$, $|L_6^+;\alpha\rangle$, $|L_6^-;\beta\rangle$ basis states in the vicinity of the L characteristic point in the first Brillouin zone of the rock-salt crystal structure, is given as [3]:

$$H=\begin{array}{c} \begin{array}{cccc} |L_6^-;\alpha\rangle & |L_6^-;\beta\rangle & |L_6^+;\alpha\rangle & |L_6^+;\beta\rangle \end{array} \\ \begin{vmatrix} E_g+\frac{\hbar^2k_\parallel^2}{2m_\parallel^-}+\frac{\hbar^2k_z^2}{2m_z} & 0 & \frac{\hbar}{m}P_zk_z & \frac{\hbar}{m}P_\parallel(k_x-ik_y) \\ 0 & E_g+\frac{\hbar^2k_\parallel^2}{2m_\parallel^-}+\frac{\hbar^2k_z^2}{2m_z} & \frac{\hbar}{m}P_\parallel(k_x+ik_y) & -\frac{\hbar}{m}P_zk_z \\ \frac{\hbar}{m}P_zk_z & \frac{\hbar}{m}P_\parallel(k_x-ik_y) & E_g+\frac{\hbar^2k_\parallel^2}{2m_\parallel^-}+\frac{\hbar^2k_z^2}{2m_z} & 0 \\ \frac{\hbar}{m}P_\parallel(k_x-ik_y) & -\frac{\hbar}{m}P_zk_z & 0 & E_g+\frac{\hbar^2k_\parallel^2}{2m_\parallel^-}+\frac{\hbar^2k_z^2}{2m_z} \end{vmatrix} \end{array} \quad (1)$$

The anisotropy between the longitudinal (*z*), $\langle 111\rangle$, and transverse ($\parallel$) directions of the rock-salt crystal structure (*x* and *y* are taken respectively along the $\langle\bar{1}\bar{1}2\rangle$ and $\langle 1\bar{1}0\rangle$ crystallographic directions) is accounted for within the difference in the effective masses of the electrons, $m_{\pm,z}^*$ and $m_{\pm,\parallel}^*$, and the bulk dipole matrix elements, $P_{0,z}$ and $P_{0,\parallel}$ [3]. The polarization-dependent optical matrix elements, $|\hat{\boldsymbol{e}}\cdot\boldsymbol{p}_{if}|^2$, of the QD required for the description of radiative transitions are obtained using the *Hellman-Feynman theorem*, where $\hat{\boldsymbol{e}}$ is the unit

light polarization vector, and $\boldsymbol{p}_{if}(\boldsymbol{k}) = (m_0/\hbar)\,\langle i|\partial H_k/\partial k|f\rangle$ is the electron-hole momentum matrix element of the structure, with $|i\rangle$ and $|f\rangle$ being the envelope functions of the initial and final states of the radiative process respectively. In order to capture the variation in material parameters between the core, shell, and surrounding colloid the radial variation of $P_{0,\|,z}$ and $m_{0,\|,z}$ are included, as well as the variation in the band edge energy of the conduction band minimum and valence band maximum. To assess the absorption properties of various QD structures we use the expression for the absorption cross section:

$$\sigma(\hbar\omega) = \frac{\pi}{nc\epsilon_0\omega}\left(\frac{e}{m_0}\right)^2 \sum_{if} \left|\hat{\boldsymbol{e}}\cdot\boldsymbol{p}_{if}\right|^2 \delta\left(E_f - E_i - \hbar\omega\right),$$

given in units of cm^2, where ϵ_0 is the permittivity of the free space, e is the electron charge, and ω is the incident light frequency. The delta function, δ, is replaced with a Gaussian function $\exp\left[-\left(\frac{x}{\sqrt{2}\Delta}\right)^2\right]/(\sqrt{2\pi}\Delta)$, defined by the phenomenological line broadening, Δ, set to x,y,z = 25meV in all structures considered. All results presented here are obtained with kppw code [4].

3. Results

The **k·p** Hamiltonian in the x- and y-directions are equivalent due to rock-salt crystal symmetry, however he z-direction produces different properties due to crystal anisotropy. The shape of the QD can break Hamiltonian symmetry. Starting from the spherical QD shape, we calculate the optical dipole matrix elements, electronic structure, wave functions, and absorption cross-sections of PbSe/PbS core-shell QDs of increasing eccentricity, via independent elongation either along the x- or z-directions. If the QD is elongated along the x-direction, keeping y- and z- radii the same, the QD shape breaks the in-plane isotropy of the **k·p** Hamiltonian. However if the QD is elongated along the z-direction, keeping x- and y- radii the same, such a shape only exaggerates the already existing anisotropy of the **k·p** Hamiltonian.

3.1. Energy levels

The elongation along a single axis increases the volume of the QD, resulting in a red shift in the energy spectra. The magnitude of this energy shift is different depending on the direction of elongation (Figure 1). For spherical PbSe/PbS QDs of core/shell diameter 15Å/25Å, the characteristic $e_0 - h_0$ transition is found to occur at an energy of 1.69eV. Elongation of the QD to 30Å/50Å in only the x (or equivalently y) direction results in a lowering of the band gap energy to 1.12eV, while the same elongation in only the z-direction reduces the band gap energy to 1.01eV. For a spherical QD of core/shell diameter 30Å/50Å, E_g = 0.80eV. This red shift of the $e_0 - h_0$ transition is a consequence of a simple increase of the confinement volume. The reduction in transition energies allows for absorption of photons of lesser energy, with the $e_0 - h_0$ optical gap energy being indirectly proportional to the dot size, allowing tuning of the absorption edge energy through choosing QDs of appropriate size. The lower $e_0 - h_0$ transitions allow for greater use of the solar spectrum, and for a potential increased efficiency of the solar cell device.

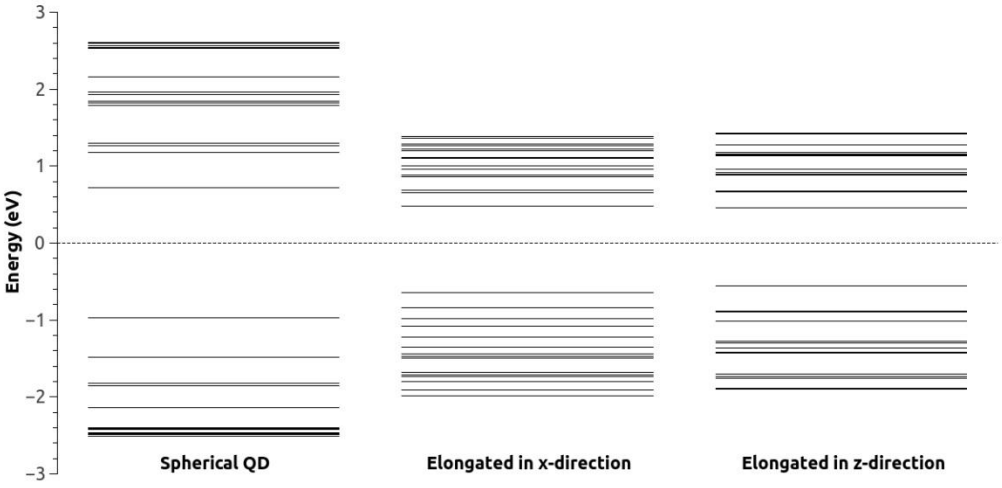

Figure 1: Energy levels for PbSe/PbS core/shell QD. Left to right, spherical, elongated in x-direction, elongated in z-direction.

3.2. Dipole elements

For the spherical core/shell structure QD, the equivalent x- and y-polarisations have identical dipole moments, occurring at the same transition energy (Figure 2), due to the isotropic crystal structure in these directions. The z-component has a lesser dipole moment. Furthermore, elongation in the x-direction causes a break in overall symmetry, resulting in an anisotropic system Hamiltonian, and different dipole moments for the x- and y-polarisations. It is also apparent there are many more optically allowed/non-vanishing transitions in the elongated samples. They are a consequence of overall symmetry breaking induced by the elongation of the QDs in certain directions (Figure 2 (b), (c)).

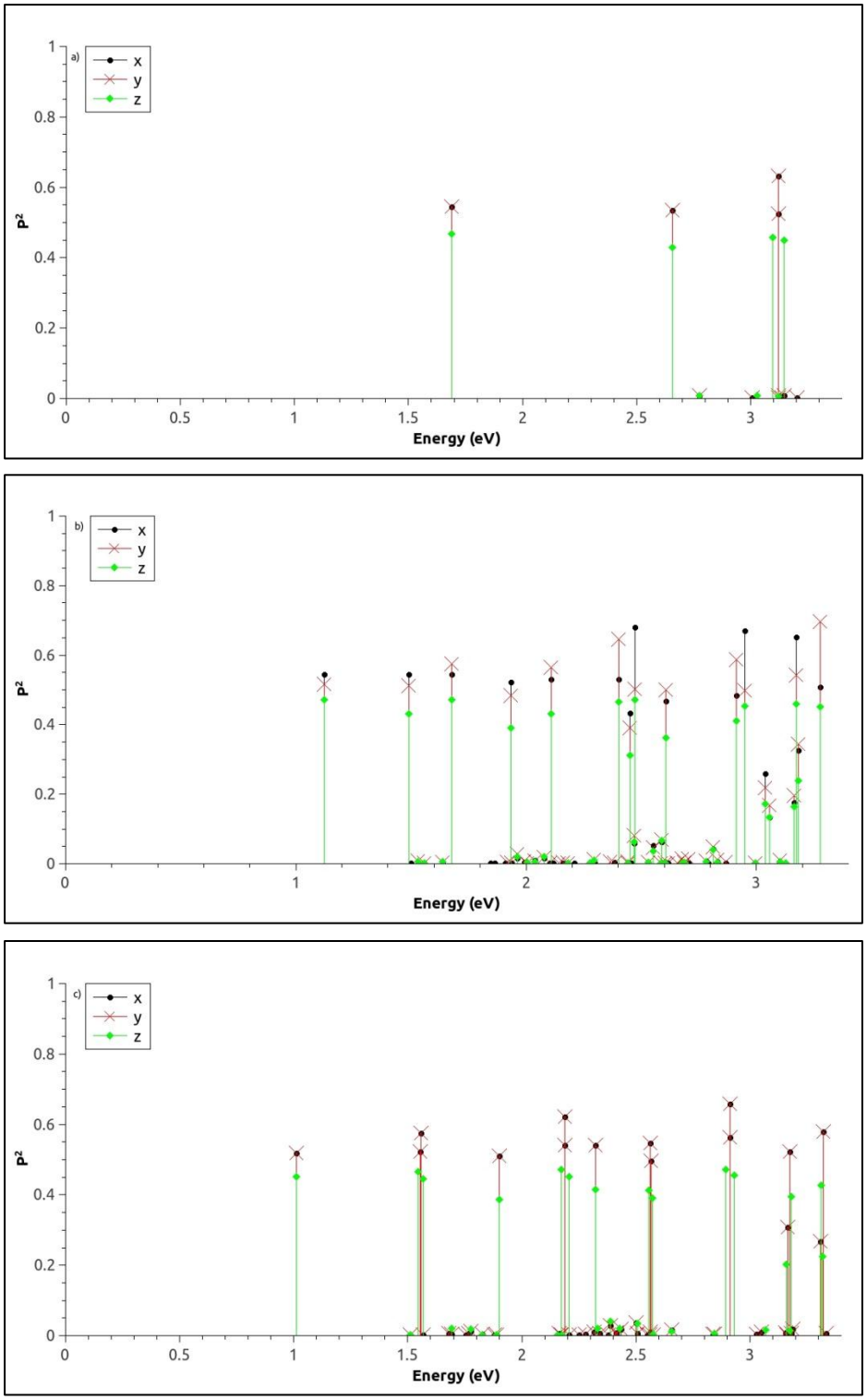

Figure 2: Dipole transitions for (a) spherical core/shell QD of diameter 15Å/25Å, (b) QD elongated in x-direction only to core/shell diameter of 30Å/50Å, and (c) QD elongated in z-direction only to core/shell diameter of 30Å/50Å.

3.3. Absorption spectra

In an ensemble of QDs, different core/shell radii are present, thus QD properties should be considered for QDs of a significant size distribution [5]. The absorption cross-section of each QD in one such distribution is shown in Figure 3. We consider nine particular QDs in the size range of core diameter 15Å-30Å and shell diameter 25Å-50Å. Figure 3 (a) represents the absorption cross-sections of QDs elongated in the x-direction with increment 1.875Å for the core and 3.125Å for the shell, while Figure 3 (b) represents cross-sections of QDs elongated in the z-direction by the same increment.

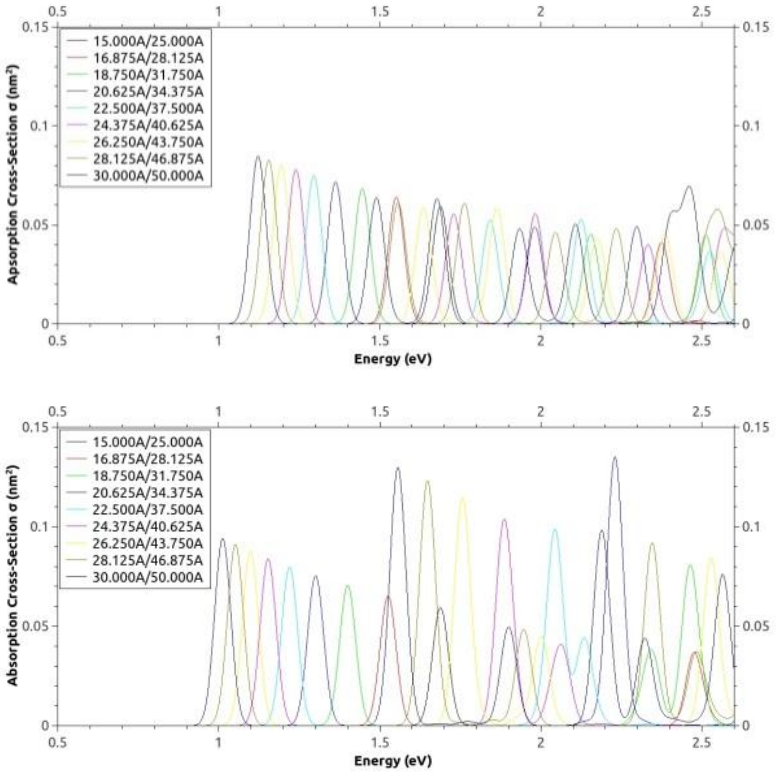

Figure 3: Absorption cross-sections in z-polarisation for QD elongation in x (top) and in z (bottom) for sample of nine QDs with core diameters 15Å-30Å and shell diameters 25Å-50Å.

An increase in dot volume results in a shift of the absorption cross-section peaks to lower energies, with a larger shift for elongation in the z-direction than for elongation in the x- or y-directions (0.68eV in the z-direction as compared to 0.57eV in the x-direction for the largest QDs). The magnitude of the absorption peaks also increases with dot volume, allowing for greater probability of absorption of lower energy photons.

4. Conclusions

The effects of eccentricity on the optical properties of ellipsoidal colloidal QDs are highly pronounced, with the direction of elongation playing a key role. Elongation in the x- or equivalent y-direction ($\langle 1\bar{1}2\rangle$ or $\langle 1\bar{1}0\rangle$ crystallographic direction) from 15Å/25Å to 30Å/50Å results in a significant reduction in optical gap energy of 0.57eV. Elongation of only the x- or y-direction introduces anisotropy, with the break in symmetry causing the x and y dipole moments to become non-identical (as compared with the in-plane isotropic spherical case). Elongation along the z-direction ($\langle 111\rangle$ direction) results in a larger reduction of the optical band gap energy of 0.82eV, along with an increase in the absorption cross-sections.

5. Acknowledgements

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